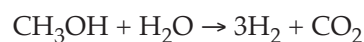


## Simulating the Structure and Properties of Magnesium Methoxide

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**M**agnesium methoxide has been intensively studied as a precursor for synthesis of inorganic materials such as perovskite-type mixed oxide phases. Here we are interested in possible uses as a hydrogen storage material. Hydrogen can be routinely generated from reacting methanol with water at high temperature in a process called steam reforming. This process can be represented as:



In an industrial setting, this reaction is catalysed by a Cu/ZnO catalyst. There is evidence that it is the strain on the copper particle caused by the ZnO support that is responsible for the catalyst activity. This study is focused on the study of the elementary chemical processes that occur when magnesium methoxide is heated or calcined.

The crystal structure of magnesium methoxide has been studied using x-ray diffraction by Starikova and coworkers [1] and consists of several structural elements. Unusually for an inorganic solid, the material is a molecular solid built of residues belonging to four types: (i)  $[\text{Mg}_4\{\mu_3\text{-OMe}\}_4(\text{OMe})_2(\text{MeOH})_{10}]^{2+}$  cations, (ii)  $[(\text{MeO})_2\text{H}]^-$  anions, (iii)  $[\text{Mg}_4\{\mu_3\text{-OMe}\}_4(\text{OMe})_4(\text{MeOH})_8]$  neutral molecules, and (iv) noncoordinating methanol molecules linked in a 3-D hydrogen-bonding framework. The crystal structure showing the packing of each of the types is shown in Fig. 1. Both the cationic and neutral species are based on the cubane-like structure, which is shown more clearly in Fig. 2.

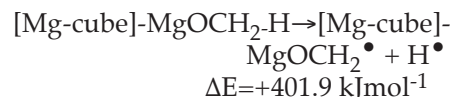
The eight vertices of the cube are formed from four OMe species and four  $\text{Mg}^{2+}$  cations. An additional three methoxide or methanol ligands complete the octahedral coordination environment around magnesium; whether these additional ligands are protonated or not determine the overall charge state of the cluster.

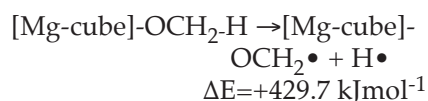
We calculated the thermodynamics of the abstraction of a hydrogen atom from various models for magnesium methoxide and also, as a baseline, from a single isolated methanol molecule. We were primarily interested in the breaking of C-H bonds, since this step must occur to ultimately form hydrogen. As a competing reaction, we also considered the breaking of the C-O bond to form a carbon radical species. The calculations were performed using the quantum chemistry software, *Gaussian03* [2]. The PBE density functional was used with a 6-31G\* basis set. The results for the isolated methanol molecule are given below:



This suggests that the C-O bond is the stronger bond in a single methanol molecule.

In the case of magnesium methoxide, we built a cluster model such that the overall charge was neutral [(unit (iii) above)]. In the case of the C-H bond breaking process, there are two possible bonds to consider corresponding to hydrogen abstraction from a methoxy species acting as an additional ligand to magnesium ( $\text{MgOCH}_2\text{-H}$ ), and also from a methoxy species forming the corner of the cube ( $\text{OCH}_2\text{-H}$ ). The results of the calculations on these models are:





We predict a slightly stronger bond in the case of the corner methoxide, although the difference is undoubtedly within the error of the calculation.

Starikova and coworkers further report that upon calcination an amorphous product is formed and speculate that the structure of this material may be related to that observed for the calcium ethoxide crystal structure determined by Turova and co-workers [3]. In this case, the dominant structural unit is a double cube with metal-oxo bridges on the shared faces as in Fig. 3.

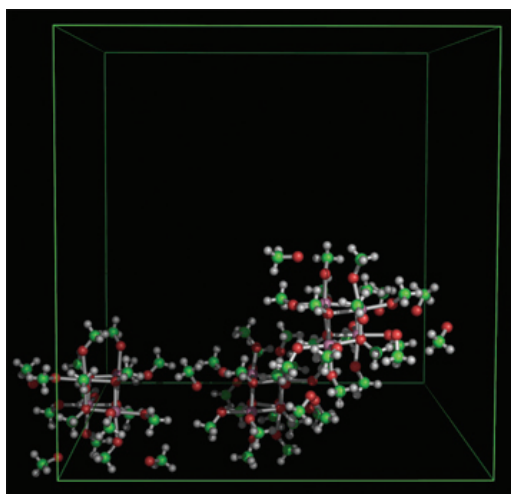
Since the calcined structure is the dominant phase in the industrial environment, we are currently performing further calculations to assess the impact of this new structural model on our calculated energies.

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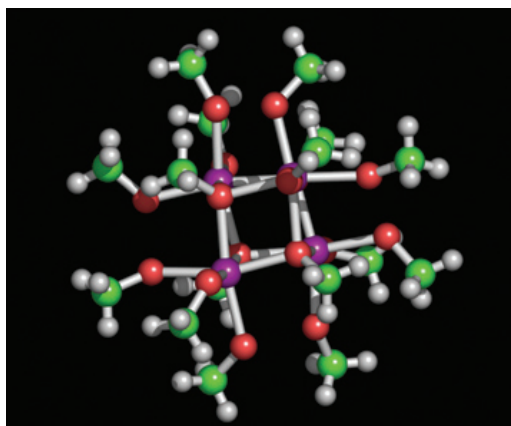
[1] Z.A. Starikova, et al., *Polyhedron* **16**, 967–974 (1997).

[2] M.J. Frisch, et al., *Gaussian 03*, Revision C.02 (Gaussian, Inc., Wallingford, CT, 2004).

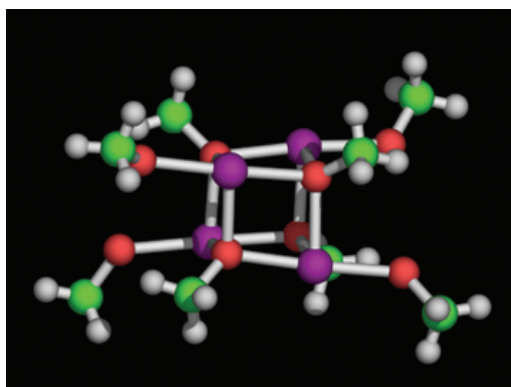
[3] N.Y. Turova, et al., *J. Chem. Soc. Chem. Comm.*, **21–23** (1993).



**Fig. 1.**  
Crystal structure of magnesium methoxide after Starikova and co-workers [1] (carbon: green, oxygen: red, hydrogen: white, magnesium: purple).



**Fig. 2.**  
The cubane-like structural unit in magnesium methoxide.



**Fig. 3.**  
Double cube model for calcined structure.